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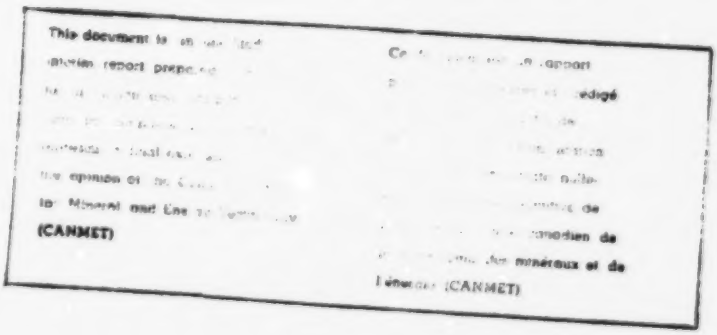
January 1987



Project: 30.69.02
Analytical Methodology

MICROMEDIA

11 pp

MINERAL SCIENCES LABORATORIES
DIVISION REPORT MSL 87-4 (TR)

THE ANALYSIS OF MILL PROCESS SOLUTIONS FOR FERROUS/FERRIC IRON RATIO, SILICON AND PHOSPHORUS BY VARIOUS ANALYTICAL TECHNIQUES

by

J.L. Dalton* and G. Hunt**

ABSTRACT

The Division of Nuclear Fuel Cycle of the International Atomic Energy Agency (IAEA) requested the assistance of CANMET Chemical Laboratory in the preparation of a manual on analytical chemistry in the uranium industry. This report, which deals with the determination of ferrous and ferric ion, silicon and phosphorus in mill process solutions, is intended to be part of this manual. For all three methods outlined in this report, extensive reference is made to CANMET monograph 881 by Elsie M. Donaldson. Users of the proposed IAEA manual will require a copy of this monograph as a working document. It is an invaluable reference work for those engaged in the analysis of ores and mineral processing products, and includes more than one hundred methods by classical and various instrumental techniques.

Key Words: Analysis, Solutions, Iron, Silicon, Phosphorus

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L'ANALYSE, PAR DIVERSES MÉTHODES, DE LA SILICE, DU PHOSPHORE ET DU RAPPORT FER FERRIQUE/FER FERREUX DANS LES SOLUTIONS PROVENANT D'UNE USINE DE TRAITEMENT

par

J.L. Dalton* et G. Hunt**

RÉSUMÉ

La Division du cycle du combustible nucléaire de l'Agence internationale de l'énergie nucléaire (AIEN) a demandé au Laboratoire de chimie de CANMET de contribuer à la préparation d'un manuel de la chimie analytique dans l'industrie de l'uranium. La présente étude, qui porte sur le dosage des ions ferreux et ferrique, de la silice et du phosphore dans les solutions provenant d'une usine de traitement, fera partie du manuel. L'étude décrit trois méthodes analytiques et renvoit souvent le lecteur à la monographie n° 881 de CANMET, par Elsie M. Donaldson. Les utilisateurs du manuel proposé de l'AIEA devront se procurer un exemplaire de la monographie comme document de travail. C'est un ouvrage de référence indispensabble pour l'analyse des minerais et des produits de traitement des minéraux, et décrit plus de cent méthodes classiques et instrumentales.

Mots clés: analyse, solutions, fer, silice, phosphore

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DETERMINATION OF FERROUS AND FERRIC IRON IN SOLUTION BY TITRATION WITH POTASSIUM DICHROMATE

This method is based on that described in Donaldson's monograph (1). After the addition of sulphuric and phosphoric acids to an aliquot of the sample solution, ferrous iron is titrated with potassium dichromate using either sodium diphenylaminesulphonate as internal indicator or potentiometrically to -480 millivolts (2). Total iron is determined in a similar manner after the reduction of the iron III present to iron II with stannous chloride. Ferric iron is determined by difference.

For details of the methods, the reader is referred to Donaldson's monograph (1). The following is an outline of the method.

REAGENTS

STANDARD POTASSIUM DICHROMATE SOLUTION, 0.1 N (16.67×10^{-3}M). Dissolve 0.8070 g of pulverized reagent - dried at 105°C for 1-2 h - in water and dilute the solution to 2 L (Note 1).

STANNOUS CHLORIDE SOLUTION, 5% m/V. Dissolve 12.5 g of stannous chloride dihydrate in 50 mL of hot, concentrated hydrochloric acid and dilute the solution to 250 mL with water. Add several pieces of tin metal and store the solution in a dark bottle.

FERROUS AMMONIUM SULPHATE SOLUTION, 0.1 N (0.1 M). Dissolve 3.9216 g of ferrous ammonium sulphate hexahydrate in 5% sulphuric acid and dilute the solution to 100 mL with the same acid solution.

SODIUM DIPHENYLAMINESULPHONATE (oxidized) INDICATOR TABLETS (0.001 g). If tablets are not available, an oxidized solution of the indicator can be prepared as follows:

Dissolve 0.27 g of sodium diphenylaminesulphonate in 100 mL of water, add 10 mL of 50% sulphuric acid and dilute the solution to 300 mL with water. Slowly add 25 mL of 0.1 N potassium dichromate solution in small increments, then add 8 mL of 0.1 N ferrous ammonium sulphate solution and

allow the resulting green mixture to stand for 3 or 4 days or until a portion of the supernatant solution no longer yields a colour with a solution containing 100 mL of 5% sulphuric acid and 2 mL of 0.1 N potassium dichromate solution. Carefully siphon off the supernatant solution, then add 300 mL of water and 15 mL of concentrated sulphuric acid and siphon off the solution again after the precipitate has settled. Centrifuge the precipitate and wash it with 5% sulphuric acid. Shake the washed precipitate with 100 mL of water, then transfer the resulting suspension to a small brown glass bottle. Shake the mixture well before use.

MERCURIC CHLORIDE SOLUTION, saturated.

SULPHURIC ACID (oxygen-free), 50% V/V. Prepare the solution with oxygen-free water.

PHOSPHORIC ACID (oxygen-free), 50% V/V. Prepare the solution with oxygen-free water.

WATER (oxygen-free). Freshly boiled and cooled water.

STANDARDIZATION OF POTASSIUM DICHROMATE SOLUTION

Transfer 0.2000 g of high-purity iron metal to a 600-mL beaker, cover the beaker, add 20 mL of concentrated hydrochloric acid and heat the solution gently until the iron has dissolved. Remove the cover, wash down the sides of the beaker with a small amount of 10% hydrochloric acid and dilute the solution to about 30 mL with the same acid solution. Heat the solution to just below the boiling point, then while stirring it, reduce the iron by adding 5% stannous chloride solution, by drops, until the yellow colour of the ferric chloride just disappears. Add 1-3 drops in excess and cool the solution to room temperature in a water-bath. Add 10 mL of saturated mercuric chloride solution, mix the solution thoroughly and then allow it to stand for approximately 5 min. Dilute the solution to about 300 mL with cold, oxygen-free water, then add 10 mL each of 50% oxygen-free sulphuric and phosphoric acids and one sodium diphenylaminesulphonate indicator tablet - or 5 drops of indicator solution - and titrate the

resulting solution immediately with standard potassium dichromate solution to a violet-blue end-point. Correct the result obtained by subtracting that obtained for a blank solution that is carried through the reduction procedure. Calculate the normality and the iron equivalent (mg/mL) of the potassium dichromate solution - 1 mL of 0.1 N potassium dichromate solution = 5.585 mg of iron.

PROCEDURE

For the ferrous determination, transfer a suitable aliquot of the sample solution to a 600 mL beaker and dilute to about 300 mL with oxygen-free water, add 10 mL each of the sulphuric and phosphoric acids and one indicator tablet, or 5 drops of indicator solution, and titrate the solution to a violet-blue end-point.

For the ferric determination, transfer an identical aliquot of the sample solution to a 600 mL beaker, add 10 mL of concentrated hydrochloric acid, heat the solution to just below the boiling point and procede with the reduction and subsequent titration as described in the standardization section. The difference between the two titrations is equivalent to the ferric ion content of the aliquot.

REFERENCES

(1) Elsie M. Donaldson "Methods for the Analysis of Ores, Rocks and Related Materials" CANMET Monograph 881 Second Edition, pp. 437-452, 1982, Energy, Mines and Resources, Canada, Ottawa, Canada K1A 0G1

(2) Personal Communication, G.A. Hunt, Chemical Laboratory, CANMET, Energy, Mines and Resources Canada, Ottawa, Canada, K1A 0G1.

DETERMINATION OF SILICON IN SOLUTION AND ACID SOLUBLE POWDERED MATERIAL BY ATOMIC ABSORPTION SPECTROPHOTOMETRY.

The atomic-absorption method described in Donaldson's monograph may be used to determine silicon in solutions(1).

REAGENTS

STANDARD SILICON SOLUTION, 500 µg/mL. Transfer 0.5345 g of pure silicon dioxide to a 30-mL zirconium crucible, add approximately 4 g of sodium peroxide from a 5-g weighed portion, mix thoroughly and cover the mixture with the remaining sodium peroxide. Cover the crucible and heat the mixture in a muffle furnace at approximately 640°C for about 30 min. Allow the melt to cool for about 5 min, then transfer the crucible and the cover to a covered 400-mL teflon beaker containing 100 mL of water. When the subsequent reaction has ceased, add 36 mL of concentrated hyrochloric acid, then remove the crucible and the cover after washing them thoroughly with water. Transfer the solution to a 500-mL polypropylene volumetric flask, dilute it to volume with water and mix it thoroughly. Immediately transfer the solution to a plastic bottle if plastic volumetric flasks are not available. The sodium concentration of this solution is approximately 6000µg/mL.

SODIUM SOLUTION, 30 000 µg/mL. Dissolve 76 g of sodium chloride in water and dilute the solution to 1 L. Store the solution in a plastic bottle.

CALIBRATION SOLUTIONS

To an appropriate number of 100-mL plastic volumetric flasks, add, by burette, suitable increments of the standard 500 µg/mL silicon solution to cover the range from 10 to 300 µg/mL. Add sufficient concentrated hydrochloric acid so that 5 mL will be present and a sufficient volume of 30,000 µg/mL sodium solution so that the resultant sodium concentration will be approximately 6000 µg/mL. Add 5 mL of concentrated hydrochloric acid and 20 mL of 30,000-µg/mL sodium solution to a separate flask; this constitutes the zero calibration solution. Dilute each solution to volume with water.

PROCEDURES

Refractory Acid-Soluble Material

Depending on the expected silicon content, decompose 0.5-2 g of powdered sample by fusing it with 5 g of sodium peroxide and dissolve and treat the melt as described in the method for the preparation of the standard silicon solution. Transfer the solution to a 500-mL volumetric flask and dilute it to volume with water.

Measure the absorbance of the resulting solution at 251.6 nm in a slightly luminous nitrous oxide-acetylene flame. Determine the silicon content of the solution by relating the resulting value to those obtained concurrently for standard silicon solutions of slightly higher and lower concentrations and containing approximately the same amount of sodium.

If dilution of the sample solution is required, transfer a suitable aliquot - up to 50 mL - to a 100-mL volumetric flask. Add sufficient concentrated hydrochloric acid so that 5 mL will be present, then add sufficient 30 000-µg/mL sodium solution so that the resultant sodium concentration will be approximately 600-µg/mL. Dilute the solution to volume with water and determine the silicon content of the aliquot as described above.

Mill Process Solutions

Transfer a suitable aliquot of the sample solution to a 100 mL plastic volumetric flask, add 5 mL of concentrated hydrochloric acid and 20 mL of 30,000 µg/mL sodium solution, dilute to volume with water and proceed with the determination of silicon as described above.

REFERENCES

(1) Elsie M. Donaldson, "Methods for the Analysis of Ores, Rocks and Related Materials", CANMET Monograph 881 Second Edition pp. 83.

THE DETERMINATION OF PHOSPHORUS IN SOLUTIONS BY THE SPECTROPHOTOMETRIC PHOSPHOVANADOMOLYBDIC ACID METHOD

Depending on the composition of the solution, phosphorus in solutions can be determined either directly by the spectrophotometric phosphovanadomolybdic acid method(1) or after separation from interfering elements by extraction of the complex in n-amyl alcohol(2). In the direct method, interferences from coloured ions is avoided by using an identical aliquot of the sample solution, not treated with ammonium vanadate and ammonium molybdate, as the reference solution(1).

REAGENTS

STANDARD PHOSPHORUS SOLUTION, 0.2 mg/mL. Dissolve 0.4584 g of anhydrous disodium phosphate (Na_2HPO_4) - dried at 105°C for 1-2 h - in water and dilute the solution to 500 mL. Store it in a plastic bottle. Prepare a 10 µg/mL solution by diluting 10 mL of this solution to 200 mL with water.

AMMONIUM VANADATE SOLUTION, 0.25% m/V. Dissolve 2.5 g of ammonium metavanadate (NH_4VO_3) in about 500 mL of water and add 20 mL of concentrated nitric acid. Allow the solution to stand overnight, then filter it, if necessary, and dilute it to 1 L with water.

AMMONIUM MOLYBDATE SOLUTION, 5% m/V. Dissolve 50 g of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}.4H_2O$] in about 500 mL of warm water. Allow the solution to stand overnight, then filter it, if necessary, dilute it to 1 L with water and store it in a plastic bottle.

NITRIC ACID 50% V/V

PERCHLORIC ACID 5% V/V

CALIBRATION CURVE

Without Extraction

Add 5 mL of concentrated, colourless nitric acid to each of eight 100-mL volumetric flasks; then, by burette, add to the last seven flasks

0.5, 1, 2, 4, 6, 8, and 10 mL, respectively, of the standard 0.2 mg/mL phosphorus solutions. The contents of the first flask constitute the blank. Dilute the contents of each flask to approximately 50 mL with water, then add 10 mL of 0.25% ammonium vanadate solution and mix the solution thoroughly. Add 20 mL of 5% ammonium molybdate solution, dilute the resulting solutions to volume with water, mix them thoroughly and allow them to stand at room temperature for approximately 30 min. Measure the absorbance of each phosphovanadomolybdic acid solution at 460 nm against the blank solution as the reference solution, using 20-mm cells. Plot milligrams of phosphorus vs absorbance.

After Extraction

Add 7 mL of 50% nitric acid and 5 mL of concentrated perchloric acid to each of six 100 mL beakers, then, by burette, add to the last five beakers 2, 4, 6, 8 and 10 mL, respectively, of the standard 10 µg/mL phosphorus solution. The contents of the first beaker constitute the blank. Dilute each solution to about 40 mL with water, heat to about 80°C, add 10 mL of 0.25 % M ammonium vanadate solution, cool the solutions to room temperature in a water-bath.

Transfer the resulting solutions to 125 mL separatory funnels and dilute to about 80 mL with water. By pipette, add 10 mL of peroxide-free n-amyl alcohol to each funnel, stopper and shake for one minute. Allow five minutes for the layers to separate, then drain off and discard the aqueous layer. Wash the extract twice by shaking it for about thirty seconds each time with 5 mL of perchloric acid. Drain the extracts into 15 mL centrifuge tubes and centrifuge for about thirty seconds. Measure the absorbance of each extract at 425 nm against n-amyl alcohol as the reference solution, using 10 mm cells. Correct the absorbance of each extract by subtracting the blank extract. Plot micrograms of phosphorus vs absorbance.

PROCEDURES

Interfering Elements Absent

Transfer two 10-40 mL aliquots of the sample solution, containing not more than 2 mg of phosphorus, to two 100 mL volumetric flasks. Transfer two identical portions of the blank solution to two more flasks, then add 5 mL

of colourless concentrated nitric acid to each flask. Dilute each solution to approximately 50 mL with water, then, omitting the addition of ammonium vanadate and ammonium molybdate solutions to one aliquot of each solution, proceed with the complex formation as described above. Measure the absorbance of the blank solution and of the sample solution against the corresponding solution, to which no ammonium vanadate and ammonium molybdate solutions were added, as the reference solution. Correct the absorbance value obtained for the sample solution by subtracting that obtained for the blank solution and determine the phosphorus content of the aliquot by reference to the appropriate calibration curve.

Interfering Elements Present

Transfer a suitable aliquot of the sample solution containing not more than 100 µg of phosphorus to a 100 mL beaker. Add 7 mL of 50% nitric acid and 5 mL of concentrated perchloric acid, then proceed with the complex formation, the extraction and the subsequent determination of phosphorus as described above.

REFERENCE

1. Elsie M. Donaldson "Methods for the Analysis of Ores, Rocks and Related Materials CANMET monograph 881, Second Edition, pp 175, 1982.

2. G.A. Hunt, R.J. Guest, J.c. Ingles, A. Hitchen and D.J. Barkley, "A Manual of Analytical Methods Used by the Canadian Mining Industry", Part 2, Extraction Metallurgy Division Report EMI74-14, pp. 104-106, 1974.